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6. AUTHORS Laurie J. Butler			5d. PROJECT NUMBER		
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14. ABSTRACT Our experiments elucidated the decomposition mechanism of energetic materials with geminal dinitro groups using 2-bromo-2-nitropropane as a photolytic precursor for two key intermediates. We used crossed laser-molecular beam scattering experiments and velocity map imaging experiments to determine the primary photodissociation channels and examine the unimolecular dissociation of the highly energized intermediates produced. Our experiments identified a novel mechanism for NO loss from nitroalkyl radicals that circumvents the traditional higher energy nitroalkyl isomerization. We computationally characterized the intrinsic reaction coordinate for					
15. SUBJECT TERMS energetic materials, TNAZ, FOX7, photodissociation, G3//B3LYP					
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## Report Title

### Final Report: Radical Reactions in the Decomposition of Energetic Materials

#### ABSTRACT

Our experiments elucidated the decomposition mechanism of energetic materials with geminal dinitro groups using 2-bromo-2-nitropropane as a photolytic precursor for two key intermediates. We used crossed laser-molecular beam scattering experiments and velocity map imaging experiments to determine the primary photodissociation channels and examine the unimolecular dissociation of the highly energized intermediates produced. Our experiments identified a novel mechanism for NO loss from nitroalkyl radicals that circumvents the traditional higher-energy nitro-nitrite isomerization. We computationally characterized the intrinsic reaction coordinate for this NO loss mechanism at the B3LYP/6-311++g(3df,2p) level of theory and calculated the transition-state energies using the G4 composite method. The subsequent dynamics en route to the highly exothermic NO + acetone product channel proceeds through a three-membered ring intermediate. The crossed laser-molecular beam scattering experiments on the 2-nitro-2-propyl radical confirmed the importance of this new mechanism in determining the product branching.

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**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

Received

Paper

- |            |      |  |
|------------|------|--|
| 02/04/2013 | 2.00 | Ryan S. Booth, Chow-Shing Lam, Laurie J. Butler. A Novel Mechanism for Nitric Oxide Production in Nitroalkyl Radicals that Circumvents Nitro-Nitrite Isomerization, The Journal of Physical Chemistry Letters, (01 2013): 547. doi: 10.1021/jz302138n                            |
| 03/04/2013 | 3.00 | Chow_Shing Lam, Matthew Brynteson, Lei Wang, Laurie Butler, Ryan Booth. Elucidating the Decomposition Mechanism of Energetic Materials with Geminal Dinitro Groups Using 2-Bromo-2-Nitropropane Photodissociation, J. Phys. Chem. A, (07 2013): 0. doi:                          |
| 10/08/2014 | 4.00 | Ryan S. Booth, Chow-Shing Lam, Laurie J. Butler. A Novel Mechanism for Nitric Oxide Production in Nitroalkyl Radicals that Circumvents Nitro-Nitrite Isomerization, Journal of Physical Chemistry Letters, (01 2013): 547. doi:  |
| 10/08/2014 | 5.00 | Ryan S. Booth, Chow-Shing Lam, Matthew D. Brynteson, Lei Wang, Laurie J. Butler. Elucidating the Decomposition Mechanism of Energetic Materials with Geminal Dinitro Groups Using 2-Bromo-2-nitropropane Photodissociation, Journal of Physical Chemistry, (03 2013): 9531. doi: |

**TOTAL: 4**

Number of Papers published in peer-reviewed journals:

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(b) Papers published in non-peer-reviewed journals (N/A for none)

Received      Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

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(c) Presentations

2011 Fall MRS meeting, symposium on “Advances in Energetic Materials Research”, Boston, MA, Nov. 28 – Dec. 2, 2011. Title: Chemical pathways of energy release in nitro compounds: The 2-nitro-2-propyl radical intermediate

Number of Presentations: 0.00

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Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received      Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received      Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

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(d) Manuscripts

Received      Paper

12/12/2012    1.00    Ryan S. Booth, Chow-Shing Lam, Matthew D. Brynteson, Lei Wang, Laurie J. Butler. Elucidating the Decomposition Mechanism of Energetic Materials with Di-Nitro Functional Groups Using 2-Bromo-2-Nitropropane Photodissociation, The Journal of Physical Chemistry A (12 2012)

**TOTAL:      1**

Number of Manuscripts:

---

Books

Received      Book

**TOTAL:**

Received      Book Chapter

**TOTAL:**

Patents Submitted

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Patents Awarded

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## Awards

Laurie J. Butler: AAAS Fellow, 2012; Fellow of the American Chemical Society, 2011.

Ryan S. Booth: NRC Postdoctoral Research Associateship Award to postdoc with Stearns at the Kirkland Air Force Base in Albuquerque, Feb 1, 2014.

### Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Ryan S. Booth	0.75	
Matthew Brynteson	0.25	
Lei Wang	0.25	
<b>FTE Equivalent:</b>	<b>1.25</b>	
<b>Total Number:</b>	<b>3</b>	

### Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Chow-Shing Lam	0.25
<b>FTE Equivalent:</b>	<b>0.25</b>
<b>Total Number:</b>	<b>1</b>

### Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Laurie J. Butler	0.20	
<b>FTE Equivalent:</b>	<b>0.20</b>	
<b>Total Number:</b>	<b>1</b>	

### Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

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### Names of Personnel receiving masters degrees

<u>NAME</u>
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Lei Wang (en route to Ph.D.)
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Ryan S. Booth (en route to Ph.D.)
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Matthew Brynteson (en route to Ph.D)
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<b>Total Number:</b>	<b>3</b>
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### Names of personnel receiving PHDs

<u>NAME</u>
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Ryan S. Booth (Jan 2014)
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<b>Total Number:</b>	<b>1</b>
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### Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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Robert Radway (under HSAP sup	1.00
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<b>FTE Equivalent:</b>	<b>1.00</b>
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<b>Total Number:</b>	<b>1</b>
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### Sub Contractors (DD882)

### Inventions (DD882)

### Scientific Progress

See attachment

### Technology Transfer

None.

## "Radical Reactions in the Decomposition of Energetic Materials"

L. J. Butler, The University of Chicago

W911NF1010314, Program Manager James Parker

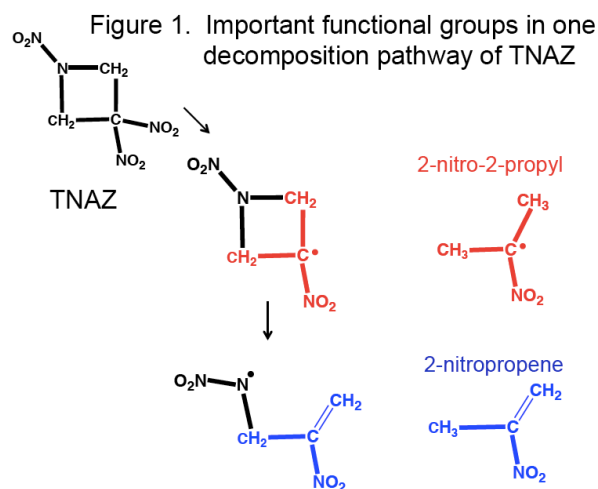
### Final Report for the ARO Funding Period 7/15/2010 – 7/14/2013

Our work in the ARO funding period from 7/15/2010 – 7/14/2013 sought to investigate the chemical mechanism for TNAZ decomposition, but our most important result was the identification of a new energy release pathway that circumvents the traditional nitro-nitrite isomerization pathway. This pathway, described later in this section, is not important for TNAZ, but is important for any energetic material that has an intermediate with an NO<sub>2</sub> group attached to an atom with an unpaired electron. That functionality may be produced by ring opening in strained ring materials or by loss of the first NO<sub>2</sub> group in geminal di-nitro energetic materials.

Our study of TNAZ began by investigating two mimetics, 2-nitro-2-propyl radical and 2-nitropropene, shown in Fig. 1 below. The experiments generated 2-nitropropene and 2-nitro-2-propyl radicals with high internal energy from 2-bromo-2-nitropropane photodissociation. Using a crossed laser-molecular beam scattering apparatus and a velocity map imaging apparatus with VUV photoionization, we first identified four competing photolysis channels. HBr photoelimination and C-Br fission

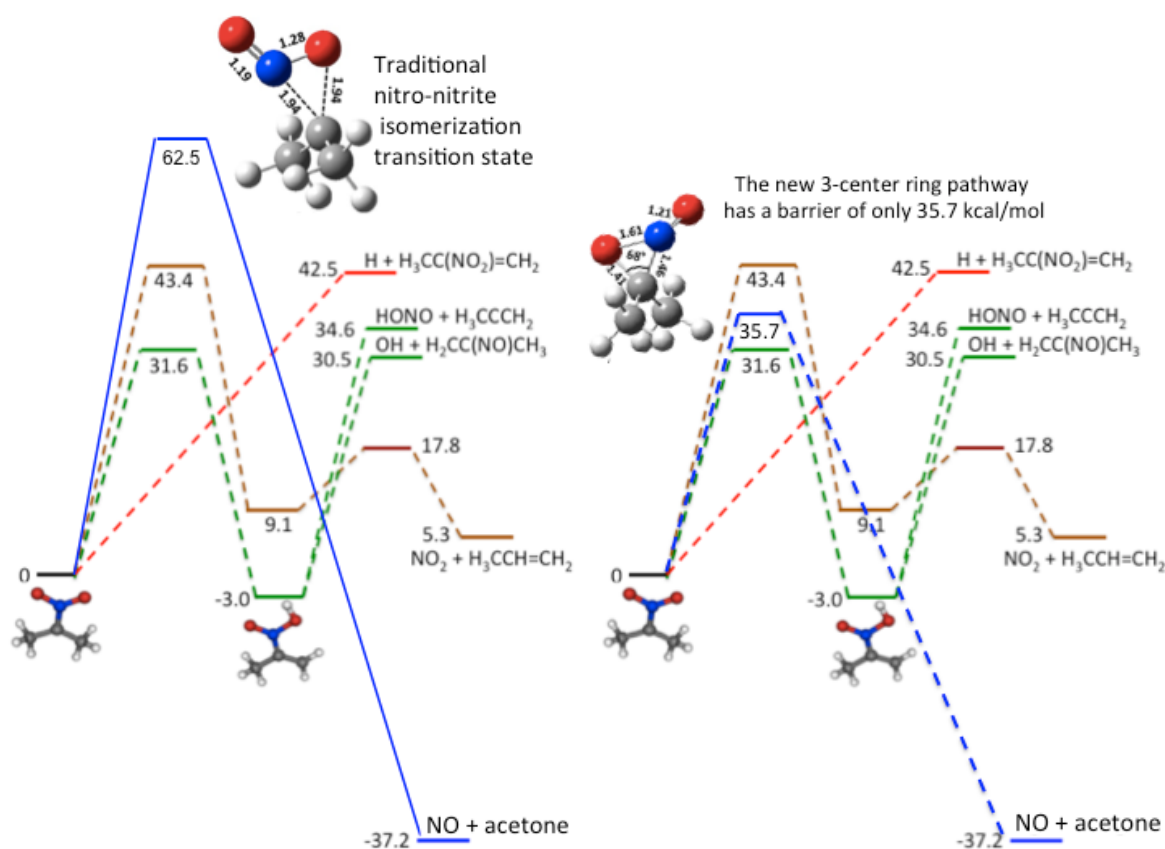
generated the species shown in Fig. 1. As reported in our full paper<sup>1</sup> we resolved the competing product channels from these intermediates, confirmed by detecting momentum-matched products. The product channels we detected from 2-nitropropene were HONO + C<sub>3</sub>H<sub>4</sub> and NO + CH<sub>2</sub>C(O)CH<sub>3</sub>, while the 2-nitro-2-propyl radical evidenced three competing dissociation channels: H + H<sub>3</sub>CC(NO<sub>2</sub>)CH<sub>2</sub>, HONO + H<sub>3</sub>CCCH<sub>2</sub>, and the highly exothermic NO + acetone product channel.

Our work was originally motivated by the need to assess the subsequent steps in the dissociation mechanism of TNAZ. Bauer and co-workers<sup>2</sup> suggested a quite different mechanism than the original put forward by Y.T. Lee and co-workers<sup>3</sup>, with the key difference being that the YT Lee mechanism suggested that primary C-NO<sub>2</sub> fission was followed by ring opening and fission of the second of the geminal C-NO<sub>2</sub> bonds. Thompson<sup>4</sup> reviewed that work in his computational study and calculated the energetic barriers for the competing decomposition pathways of several of the intermediate species generated en route in TNAZ decomposition to assess the proposed mechanisms. Our experiments are in agreement with Thompson's results



(fission of the second C-NO<sub>2</sub> bond is not competitive), but our study of the 2-nitro-2-propyl radical revealed a fascinating exothermic pathway to NO product that, though not relevant to TNAZ, is the crucial energy release step in many nitro-containing radical intermediates. Some of the work in the current proposal focuses on this pathway, so we review it below.

In our experiments on the decomposition pathways of the 2-nitro-2-propyl radical, we were initially surprised to see the substantial signal from the NO + acetone product channel. We had calculated the energetic barriers to each decomposition pathway by finding transition states for each channel that were similar to analogous nitro compounds. We found a transition state for the NO + acetone product channel that was very similar to the nitro-nitrite isomerization pathway identified by many other workers for nitroalkanes. It is shown in the left frame of Fig. 2 below; both the C-N and the newly forming C-O bond are extended to near 2 Å at the transition state. However, in the 2-nitro-2-propyl radical, there are two other competing product channels with much lower barriers (20 kcal/mol lower!) so it was surprising to see any substantial NO + acetone products. Further computational effort identified a novel transition state, one that is only possible for nitro compounds with an unpaired electron on the atom to which the NO<sub>2</sub> is bonded. This pathway proceeds through a 3-membered ring intermediate shown in the right frame of Fig. 2 below, and has a barrier that is much lower (by over 25 kcal/mol).





Thus it is consistent with our experimental observation of the NO + acetone product channel. Our letter<sup>5</sup> reporting this new pathway to exothermic NO loss suggests it is a dominant one in geminal dinitro energetic materials. Our preliminary work on FOX-7 begun during the grant period indicated that the most exothermic product channel from the radical produced upon loss of the first NO<sub>2</sub> evidences an analogous transition state for highly exothermic NO loss.

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- <sup>1</sup> Elucidating the Decomposition Mechanism of Energetic Materials with Geminal Dinitro Groups Using 2-Bromo-2-Nitropropane Photodissociation, R. S. Booth, C. –S. Lam, M. D. Brynteson, L. Wang, and L. J. Butler, J. Phys. Chem. A, <http://dx.doi.org/10.1021/jp312248v> (2013).
- <sup>2</sup> Gas Phase Pyrolysis of 1,3,3-Trinitroazetidine: Shock Tube Kinetics, Y. –X. Zhang and S. H. Bauer, J. Phys. Chem. A 102, 5846-5856 (1998).
- <sup>3</sup> Studies of Initial Dissociation Processes in 1,3,3-Trinitroazetidine by Photofragmentation Translational Spectroscopy, D. S. Anex, J. C. Allman, and Y. T. Lee, in *Chemistry of Energetic Materials*, ed. by G. A. Olah and D. R. Squire (Academic Press, New York, 1991), pp. 27-54.
- <sup>4</sup> Theoretical Predictions of the Decomposition Mechanism of 1,3,3-Trinitroazetidine (TNAZ), S. Alavi, L. M. Reilly, and D. L. Thompson, J. Chem. Phys. 119, 8297-8304 (2003).
- <sup>5</sup> A Novel Mechanism for Nitric Oxide Production in Nitroalkyl Radicals that Circumvents Nitro-Nitrite Isomerization, R. S. Booth, C. –S. Lam, and L. J. Butler, J. Phys. Chem. Lett. 4, 547-550 (2013).